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SAMPLING AND ANALYSIS OF SOILS FOR PLUTONIUM

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Abstract

This paper describes the progress in analysis of soils artificially spiked with plutonium, soils containing particulate plutonium deposited from a processing plant, and soils containing fallout plutonium. The emphasis is on distribution of the actinide determined after both fusion and acid leaching techniques.

The residue from multiple evaporations of soil with hydrofluoric acid is fused with potassium fluoride and potassium pyrosulfate, dissolved in dilute sulfuric acid, and the solution is evaporated to remove fluorides. Plutonium is then extracted with a hydrochloric acid solution with tri-isootylamine (TIOA) and stripped from TIOA with dilute acid. Plutonium is coprecipitated with LaF_3, the precipitate is filtered onto a 0.2-micron polycarbonate filter membrane and the plutonium is counted in an alpha spectrometer.

Recovery, indicated by ^{236}Pu tracer added to each sample, is 75 ± 6 percent for 5-gram soils. Recovery is higher for smaller samples. Assays of five interlaboratory cross-check soils in the range 0.5 to 16.0 pCi/g yielded an average error of only 3.6 percent by this method.

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Introduction

There are a number of problems associated with the analysis of plutonium isotopes in soil samples. These problems can be attributed to one or both of the following conditions:

1. The plutonium may be of a refractory nature and not easily separated from the soil matrix.
2. The mode of distribution of the plutonium could have produced erratic and nonuniform dispersion of the radionuclide in the soil.

A number of fusion procedures have been developed to insure dissolution of refractory components including plutonium from soil samples. These methods, however, are limited to soil sample sizes of 10 grams or less.

Analysis of small soil samples by fusion can result in misleading data dependent upon the degree of nonuniformity of the plutonium at the sampling site. In order to overcome this difficulty, larger soil samples have been leached with various acid mixtures.

This paper describes a fusion procedure used at this Laboratory for plutonium analysis in soil samples. Results of the procedure are

compared with various acid leach procedures performed on identical soil samples

Experimental

Fusion of Soil

Initial experiments using the reagents potassium carbonate, sodium carbonate, sodium tetraborate decahydrate, barium sulfate, potassium hydroxide and others in various combinations were not successful in this Laboratory. The reagents showing the most promise were those used by Sill[1] for ^{210}Pb analysis of soil. Variations of these reagents yielded a fused sample that was completely soluble in 6N HCl. The procedure is as follows:

1. Add 5 g of dried, seived, and muffled (550°C) soil to a teflon beaker. Add ^{236}Pu tracer.
2. Add 35 ml of 28N HF and evaporate to dryness at low heat. Repeat three more times to volatilize the silica. Finally, add 15 ml of 12N HCl and evaporate.
3. Transfer the powdery residue to a 50-ml platinum crucible with the aid of a policeman.
4. Add 4 g of KF. Place a platinum top on the crucible and fuse over a meker burner for 30 minutes. Add 7.5 g of $K_2S_2O_7$ and fuse for an additional 30 minutes.

5. Cool the crucible in an ice bath, add 15 ml of 12N HCl and evaporate. Add 30 ml of water, heat and transfer to a beaker.
6. Rinse the crucible with a portion of 200 ml of 6N H_2SO_4 added to the beaker. Evaporate past the white SO_3^- fumes to remove all traces of F^-.

Purification with TIOA

The liquid ion exchanger tri-isooctylamine (TIOA) reported previously[2] was used to separate the plutonium isotopes from calcium and other trace elements in soil as well as natural uranium. The procedure is as follows:

1. After removal of fluorides, dissolve the residue in 6N HCl with heat. Use the total volume of 400 ml 6N HCl, including rinse, to transfer the solution to a separatory funnel. Add 10 drops of 50% H_2O_2 to adjust the Pu to valence (IV).
2. Add 25 ml of 10% TIOA-xylene and shake briefly. Invert the funnel and release the pressure. Shake the solutions for one minute.
3. Drain and discard the aqueous solution. Rinse the organic layer with 25 ml of 6N HCl and discard the rinse solution.
4. Strip the Pu from TIOA with two 25-ml volumes of 4N HCl-0.05N HF, shaking for two minutes each strip. (Uranium may then be stripped from the TIOA with 0.1N HCl and analyzed separately.)

5. Add 10 ml of 16N HNO_3 to the combined strip solutions and evaporate to dryness. Further wet ash the residue with 5 ml of 12N HCl plus 5 ml of $HClO_4$.

Coprecipitation and Counting

Plutonium is coprecipitated with a trace amount of LaF_3 [3] and filtered onto either a polycarbonate filter membrane (Nuclepore) or a solvinert membrane (Millipore). The automatic low-background alpha spectrometer was described previously.[4] The procedure is as follows:

1. Dissolve the wet-ashed residue in 10 ml of 1N HCl, heating to about 60°C.
2. Cool the solution to room temperature and add 1 drop of 50% H_2O_2 to adjust Pu to (IV).
3. Add 0.1 mg of lanthanum (lanthanum nitrate dissolved in 1N HCl) and 2 ml of 3N HF and allow the precipitate to form for 30 minutes.
4. Filter in a Millipore apparatus onto a 25-mm 0.2 micron membrane. Wash the beaker with water and then with alcohol.
5. Mount the filter membrane on double-faced adhesive tape attached to a 30-mm planchet.
6. Count the sample for 1000 minutes in the alpha spectrometer.
7. Calculate the quantity of plutonium isotopes and correct for the recovery of the known ^{236}Pu added initially.

Leaching Experiments

A soil sample was spiked with ^{238}Pu. The sample was dried, muffled, and thoroughly mixed and analyzed by the fusion procedure.

Duplicate leaching experiments were conducted with six solutions. One-gram samples of soil were heated to boiling with 10-ml volumes of leach solution and then allowed to digest for one hour. They were then filtered and the filters were washed with hot water until the total volume for each sample was 20 ml. One-ml aliquots were analyzed by liquid scintillation counting. Results are shown in Table 1. Note that the HCl leaches were more complete. Subsequent tests on a variety of soils, including those mentioned in the next section, showed that HF is often required for complete leaching.

Results and Discussion

Figure 1 shows the alpha spectrogram obtained by analysis of a soil through the fusion procedure using the polycarbonate membrane. Note the good resulution of ^{236}Pu, ^{238}Pu, and ^{239}Pu, which allows the quantitative determination of the isotopes.

Table 2 shows good precision and accuracy of analysis of five interlaboratory soils by the fusion method. Although the fusion method and subsequent chemical separation is described for 5-g samples of soils, it has been employed for different quantities of soil. The fusion of more than 10 g of soil appears impractical with this procedure.

Analysis of 20 environmental soils from Montgomery, Alabama and Cape Kennedy, Florida, resulted in ^{236}Pu recovery of 75 $\pm$ 6%. These

5-gram samples assayed between less than sensitivity (.03 dpm) to 0.08 dpm/g ^{239}Pu.

One concern in analysis of soil is the distribution of plutonium particles and, therefore, the proper techniques for sampling and the optimum amount of sample required for representative analysis. To investigate these factors, a soil was obtained from a nuclear processing plant where ^{239}Pu had been deposited in particulate form by accident approximately one year before receiving the soil. The particles had been covered with approximately 12 inches of fresh soil during the year prior to sampling.

The soil was dried, muffled at 550°C and thoroughly mixed prior to analysis of 21 one-gram samples by the fusion method. The recovery of ^{236}Pu was 81.6 $\pm$ 8.3% with maximum and minimum recoveries of 99% and 64%. The ^{239}Pu in the soil was 0.57 $\pm$ .40 dpm/g; however, with maximum and minimum assays of 1.72 and 0.25 dpm/g. The relative standard deviation was $\pm$ 70% compared to only 8% for the added tracer.

Twenty gram batches of the above soil were leached with a total volume of 200 ml of solution in the manner described in the Experimental Section. Ten-ml aliquots, representing 1 g of soil, were analyzed by the TIOA exchange procedure. Results are shown in Table 3. Note ahat these analyses show the HCl-HF leaches yield ^{239}Pu assays very close to the mean of the 21 fusion assays.

Summary

1. A fusion method is described which yields accurate plutonium results for small samples (1 to 10 g) of soil.
2. The distribution of particulate plutonium deposited accidentally on soil can vary almost tenfold from gram to gram.
3. Analysis of a relatively large portion of the particulate soil after acid leaching results in less variation in replicate analysis than the analysis by fusion of one-gram aliquots.
4. No leach experiments were performed on actual atomic debris plutonium; therefore, no claim is made that the highly refractory plutonium in fallout is soluble in the various leach solutions.

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Table 1

LEACHING EXPERIMENTS OF SOIL CONTAINING
1700 DPM ^{238}PU PER GRAM

Leach Solution	^{238}Pu dpm/gram Sample 1	Sample 2
Water	0	0
4N HCl	1520	1600
12N HCl	1520	1600
1N HF	0	0
28N HF	80	220
4N HCL- -1N HF	740	720

Table 2

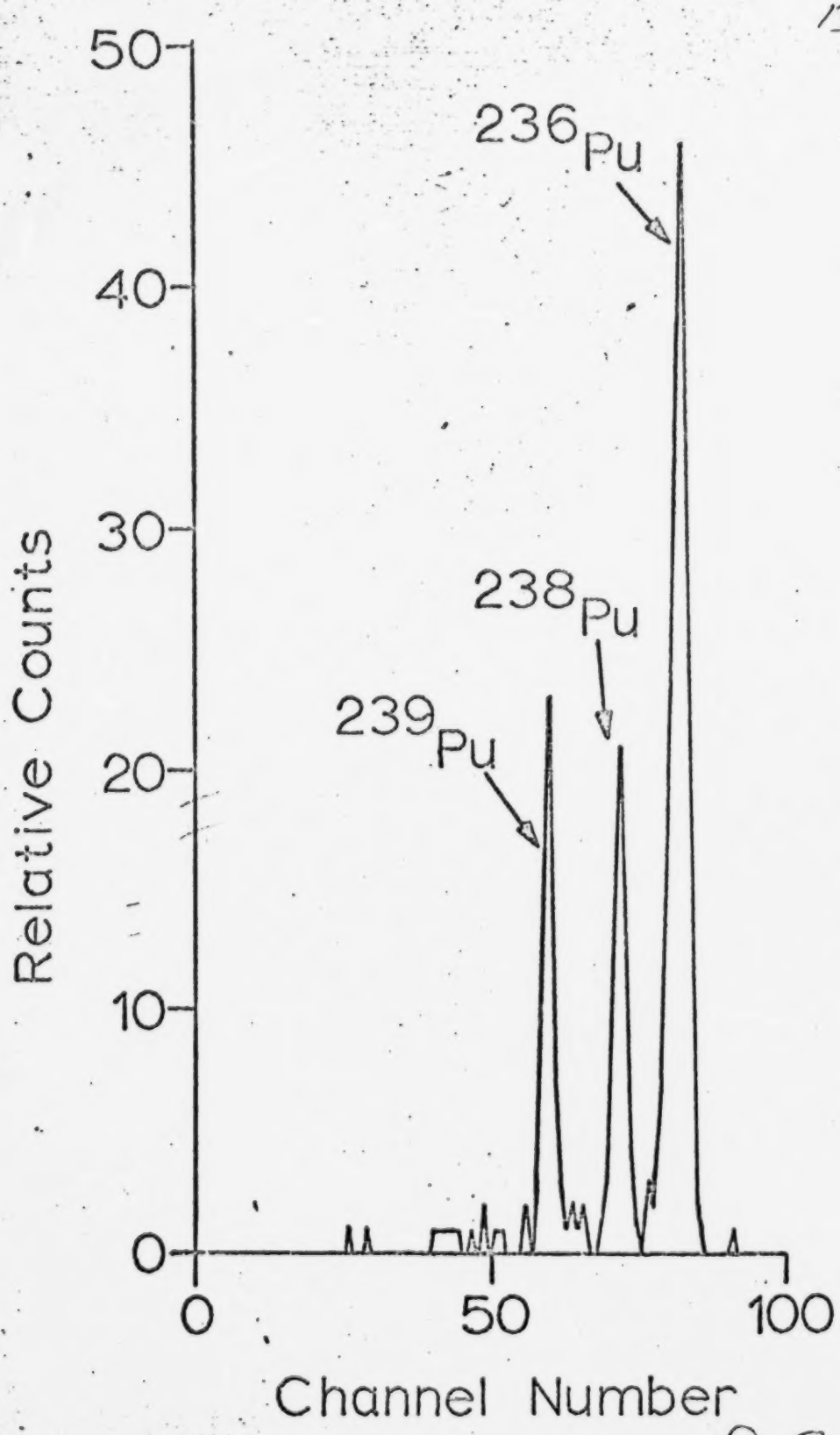
RESULTS OF PLUTONIUM IN SOIL CROSS CHECKS

Sample Number	EERL (pCi/g) ^{238}Pu	EERL (pCi/g) ^{239}Pu	KNOWN (pCi/g) ^{238}Pu	KNOWN (pCi/g) ^{239}Pu	ERROR, PERCENT ^{238}Pu	ERROR, PERCENT ^{239}Pu
1	.407	15.80				
	.319	15.90				
	.306	15.60				
Avg.	.344	15.77	.26	15.68	24.5	0.6
2	---	.031				
		.032				
		.030				
Avg.	---	.031	---	.031	---	0.0
3	---	2.43				
		2.56				
		2.31				
Avg.	---	2.43	---	2.24	---	8.5
4	---	16.98				
		16.36				
		15.69				
	Avg.	16.34	---	15.59	---	4.8
5	---	0.52				
		0.52				
		0.45				
Avg.	---	0.49	---	0.47	---	4.2
						3.6 Avg.

Table 3

LEACHING TESTS USING SOIL CONTAINING PARTICULATE ^{239}PU

Leach Solution	^{239}Pu Assay (dpm/g) Sample 1	Sample 2
4N HCl	0.22	0.22
4N HCl - 1N HF	0.57	0.42
4N HCl - 2N HF	0.64	0.69



Alpha Spectrogram of Soil